38. INCOMPATIBLE TRACE-ELEMENT GEOCHEMISTRY AND $^{87/86}$Sr IN BASALTS AND CORRESPONDING GLASSES AND PALAGONITES

Hubert Staudigel,[1] Frederick A. Frey, and Stanley R. Hart, Center for Geoalchemy,
Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts

ABSTRACT

Basalts from Sites 417 and 418 are relatively depleted in light REE compared to a chondritic REE distribution. In the least altered samples, K, Rb, Cs, and Sr and Ba concentrations are lower than in average mid-ocean ridge basalt (MORB). Thus, the source rock for these basalts must have been highly depleted in incompatible elements. However, $^{87/86}$Sr ratios in these basalts, even in microscopically fresh glass, are high (> 0.7030). These ratios, compared to normal MORB, are largely an effect of low-temperature alteration. Sr isotope exchange with sea water is postulated for basaltic glass ($^{87/86}$Sr = 0.70301) with low incompatible-element abundances, but we cannot eliminate the possibility that these relatively high $^{87/86}$Sr ratios are primary.

By studying closely associated glass-palagonite-crystalline rock samples, we can identify two types of alteration processes: (1) palagonite formation which causes loss of REE elements, without changing their distribution, and decreasing K/Rb and K/Cs with increasing K content; and (2) glass-sea water exchange which is apparently a diffusion-controlled process, causing increasing K/Rb and K/Cs with increasing K content but not affecting REE.

INTRODUCTION

The occurrence of abundant glass and olivine in Holes 418A and 417D shows that basalts can remain relatively unaltered for over 100 million years. However, greatly altered samples have been recovered from breccia zones and in the upper portions of the individual holes. Thus, basalts from these sites provide an excellent opportunity for studying primary magmatic and secondary alteration processes. In conjunction with major oxide studies by Staudigel et al. (this volume), Byerly and Sinton (this volume), and a δ^{18}O study by Muehlenbachs (this volume), a subset of their samples was analyzed for REE, Co, Cr, Sc, Hf, Sr, Ba, K, Rb, Cs, and $^{87/86}$Sr. In order to examine fresh-rock compositions and alteration processes in these rocks, glass separates and corresponding palagonites were analyzed in addition to 20 whole-rock samples.

EXPERIMENTAL TECHNIQUE

We prepared all samples, except Sections 418A-65-1, 418A-65-6, and 418A-42-3, which were provided as powders by K. Muehlenbachs. The whole-rock samples were cleaned of surface alteration and vein material, crushed in an aluminum-oxide jaw crusher, ground in an agate mill to < 200 mesh, and homogenized for 15 minutes. In order to compare glasses and palagonites with the corresponding whole rock, many whole-rock samples were

chosen next to the glassy margin of pillows. In these cases, the whole-rock samples often contain considerable amounts of interstitial glass or palagonite.

Glassy margins and palagonite veins were crushed in a steel percussion mortar, sieved, and pure separates were hand picked. The grain size of the starting material for hand picking varied from ~1 mm (palagonite) to <1 mm (for "massive" glassy selvages — Section 42-3) to <0.5 mm (for more altered, broken glassy margins — Sections 15-1 and 86-5). The hand-picked separates were cleaned ultrasonically in pure water (palagonite) or pure acetone (glass). For palagonite concentrates, only massive-looking, very fine grained homogeneous material without apparent phenocrysts was hand picked. However, palagonite is not transparent at 1 mm grain size; therefore, minor amounts of microphenocrysts may have been included in these separates. For glass concentrates, only phenocryst-free, transparent, homogeneous, and isotropic grains were selected; thus all phenocrysts were eliminated. Surfaces with smooth grooves and pits, quite unlike typical fresh broken glass surfaces, were frequently observed. These were interpreted as "fronts of palagonitization"; that is, interfaces between palagonite and "fresh" glass. We tried to eliminate grains with such surfaces by three successive steps of hand picking, resulting in our glass A sample. However, to determine the influence of such surfaces on chemical parameters, additional "impure" glass splits (glass B) containing such grains were studied.

Samples were analyzed by instrumental neutron activation for REE, Co, Cr, Sc, and Hf. A description of the techniques used can be found in Frey et al. (1974). In Table

1, we present the analyses of standard rocks and estimated errors for REE. Analyses of alkalies, Sr, Ba, and $^{87/86}$Sr were performed by isotope dilution and high-precision mass spectrometry. A detailed description of this technique has been published in Hart and Brooks (1974). Analyses of the interlaboratory comparison Sample AII 92-29-1 are included in the data set presented by Staudigel (this volume).

EXPERIMENTAL RESULTS

Rare-Earth Elements

REE, Cr, Hf, Sc, and Co were determined on 11 whole-rock samples (Table 2, Figure 1a,b, this chapter and tables 3 and 4 in Staudigel et al. [this volume]) and on three glass-palagonite pairs (Table 3, Figure 2). Chondrite-normalized REE distributions for the whole rocks (Figure 1a, b) are relatively depleted in light REE (La 3.5 to 8× chondrites and heavy REE 10 to 20× chondrites) and are typical for MORB (e.g., Bryan et al., 1976). Major- and trace-element composition of all samples analyzed for REE are given in Staudigel et al. (this volume). $\delta^{18}O$ analyses are published by Muehlenbachs (this volume). Samples from Hole 418A display a wider range of REE abundances than samples from Hole 417D which fall into the upper part of the Hole 418A range. This is consistent with all samples from Hole 417D having TiO₂ contents >1.25 wt. %, whereas samples from Hole 418A analyzed for REE have a wider range of TiO₂ abundances (0.99 to 1.56 wt. %). The variation in absolute REE abundance at each site probably reflects fractional crystallization and phenocryst redistribution (Staudigel et al., this volume) and alteration processes. In particular, for two examples (Sample 418A-73-1, 127 cm and Sample 418A-86-5, 29 cm) we studied adjoining glass-crystalline rock pairs and found that the crystalline samples have parallel REE distributions, but lower absolute REE abundances (Figure 3).

These results demonstrate the diluting effect of the cumulate phenocrysts in these crystalline samples (Staudigel et

TABLE 1
Analyses of Interlaboratory Standards —
Means and Standard Deviations of
Two Analyses by Different Analysts
in Same Laboratory

	Sample AII 92-29-1[a]	Sample BHVO-1[b]
La	3.88	14.8 ±0.5
Ce	12.6 ±1.4	35.4
Nd	11.8 ±0.6	21.9
Sm	4.16 ±0.06	5.99 ±0.10
Eu	1.45 ±0.10	2.03 ±0.13
Tb	0.83 ±0.05	0.84 ±0.02
Ho	1.45 ±0.07	1.0
Yb	3.90 ±0.03	2.06 ±0.03
Lu	0.59 ±0.01	0.31 ±0.02
Th	0.3	1.2
Cr	236 ±1	289 ±6
Co	40 ±1	46 ±2
Ta	0.5	1.1
Hf	3.3	4.8

[a]Staudigel (this volume).
[b]Flanagan (1976).

TABLE 2
REE in Basalts From Sites 417 and 418 (in ppm)

| Sample (Interval in cm)	417D-26-3, 40	417D-49-2, 23	417D-60-6, 50	417D-69-1, 122	418A-15-2, 0	418A-22-1, 46	418A-42-3, 68	418A-62-4, 104	418A-73-1, 127	418A-76-2, 99	418A-80-2, 123	418A-86-5, 29
La	2.42	2.36	1.85	2.08	1.74	1.72	1.21	2.67	1.93	1.67	1.56	1.76
Ce	7.2	6.3	6.1	6.2	—	5.5	4.4	8.52	—	5.5	5.8	6.2
Nd	8.7	7.0	5.9	8.9	—	6.9	5.6	9.4	—	4.8	7.1	7.1
Sm	—	3.33	2.79	2.39	2.36	2.08	2.21	3.48	2.51	2.09	2.40	2.38
Eu	1.26	1.20	1.05	0.991	0.994	1.12	0.811	1.180	1.05	0.81	0.94	0.94
Tb	0.83	0.74	0.62	0.58	0.60	0.56	0.56	0.78	0.64	0.55	0.68	0.63
Ho	—	1.15	0.93	0.77	0.83	0.77	0.69	1.3	0.86	0.88	0.94	0.92
Yb	3.59	2.89	3.10	2.91	2.62	2.44	2.63	3.72	2.80	2.10	2.68	2.52
Lu	0.53	0.43	0.42	0.44	0.38	0.40	0.34	0.56	0.40	0.33	0.41	0.38
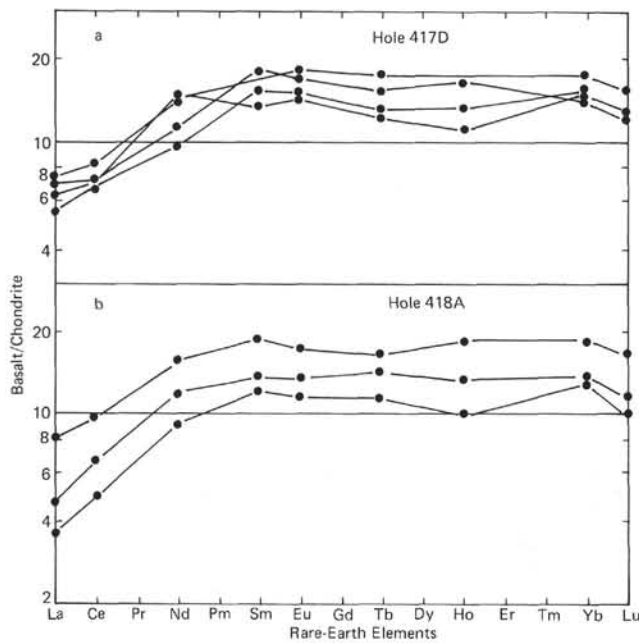
Figure 1. *(a) REE patterns of basalts from Hole 417D. (b) Some characteristic REE patterns of basalts from Hole 418A. The patterns give the approximate range of REE abundances for this hole.*

al., this volume). Despite the overall abundance of plagioclase phenocrysts, we observed only one sample with a significant Eu anomaly (Section 418A-22-1). Even though this sample has a lower Al_2O_3 content (Staudigel et al., this volume) than would be expected from accumulation of large amounts of plagioclase, the Eu anomaly is consistent with this sample showing the largest amount of modal plagioclase (32 vol. % phenocrysts). The rare occurrence of Eu anomalies in rocks from Sites 417 and 418 is in agreement with the high An-content of plagioclase phenocrysts (see Staudigel et al., this volume). Anorthite-rich feldspars do not show marked Eu anomalies.

Staudigel et al. (this volume) studied the effects of phenocryst accumulation in glass-whole-rock pairs from Holes 417D and 418A. They distinguished a "MgO-depletion trend," caused mainly by plagioclase accumulation, and a "MgO-enrichment trend," dominated by the accumulation of olivine. We have data for two glass-whole-rock pairs exhibiting the MgO-depletion trend. These whole rocks show a similar degree of depletion in REE (Figure 3), independent of varying amounts of modal cpx (Section 418A-73-1, 4 vol.%; Section 418A-86-5, 1 vol. %).

All three glasses are relatively depleted in light REE (Figure 2), and their range in absolute REE content correlates with TiO_2 abundance (Table 3). Qualitatively, this increase in REE content with increasing TiO_2 abundance is consistent with the fractionation of olivine, clinopyroxene, and plagioclase proposed by Byerly and Sinton (this volume) and Staudigel et al. (this volume).

To study the effects of glass alteration on REE abundances, we analyzed pure and impure glass separates (Glass A and B, respectively) from Sample 418A-42-3, 17 cm. Although glasses A and B have significant differences in alkali metal abundance and $^{87/86}Sr$ ratio, their REE contents are identical within experimental error (counting statistics) and the average is presented in Table 3. Also, three glass-palagonite pairs were analyzed (Table 3). The chondrite-normalized REE patterns of glass and corresponding palagonites are sub-parallel, but all the palagonites have lower (0-40%) REE concentrations than the glasses (Figure 4). Within the limits of our precision, none of the REE is preferentially depleted during palagonitization. The amount of REE depletion in the palagonites shows a (positive) correlation with alkali enrichment (Table 4), but the maximum depletion of ~40 wt. % cannot be explained by the mere dilution of the glass by hydration and alkali addition. Evidently, REE are mobilized from the glasses during the formation of palagonite. This is not surprising in light of the near-total loss of CaO during palagonitization (e.g., table 7 of Frey et al., 1974). Our results indicating loss of REE during palagonite formation are similar to those of

TABLE 3
REE, Cr, Hf, Sc, and Co in Glass/Palagonite Pairs From Hole 418A (in ppm)

Sample (Interval in cm)	418A-42-3, 17		418A-73-1, 127		418A-86-5, 29	
	Glass	Palagonite	Glass	Palagonite	Glass	Palagonite
La	1.54	0.97	–	–	2.31	1.61
Ce	4.4[a]	–	6.6	5.8	9.4	7.2
Nd	4.2[a]	–	6.1	4.3	8.6	7.2
Sm	2.39[a]	1.34	2.35	2.01	–	2.64
Eu	0.950[a]	0.645	1.25	1.07	1.390	1.055
Tb	0.64[a]	0.44	0.80	0.80	0.71	0.54
Ho	1.0	–	1.2	0.9	–	0.8
Yb	3.2	2.6	3.7	3.3	3.5	3.0
Lu	0.46	0.40	0.54	0.44	0.43	0.34
Cr	384[a]	318	–	219	378	300
Hf	1.35[a]	1.16	1.88	1.97	1.20	0.91
Sc	46.61[a]	38.6	48.2	48.4	54.8	44.7
Co	45.1[a]	30.4	45.2	38.5	44.2	36.9
TiO_2[b]	1.14		1.48		1.32	

[a] Average from double determination.
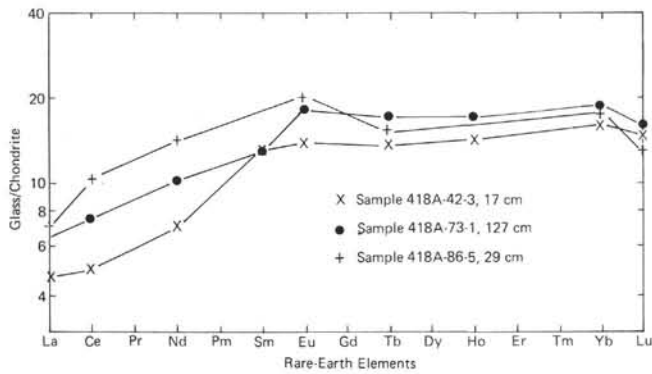[b] Taken from Byerly and Sinton (this volume).

Figure 2. *Chondrite-normalized REE patterns in pheno-cryst-free glasses from Hole 418A.*
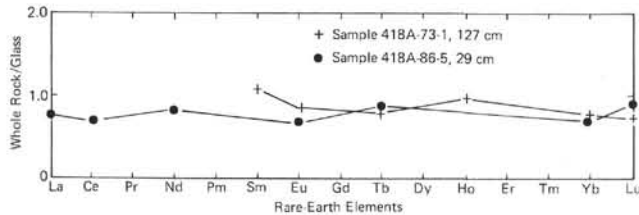

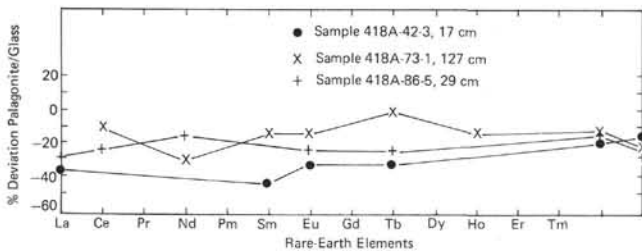Figure 3. *Whole-rock/glass REE ratios in samples from Hole 418A.*

Figure 4. *Per cent deviation of REE concentrations in pala-gonite from concentration in glasses (wt. ratio).*

Frey et al. (1974), figure 8) except that we do not find anomalous behavior for Ce. We have not observed the large

relative enrichment in light REE found by Ludden and Thompson (in press a,b) in palagonitized rinds of dredged basalts from 23°N. There are several possible explanations for these differing results for REE mobility during palagonitization:

1) Ludden and Thompson (in press a, b) studied altered rinds of *dredged* pillows, whereas we studied *drilled* samples from considerable basement penetration. While water circulation within the crust ceases shortly after its formation (Hart and Staudigel, 1978), dredged samples are open to sea water during their lifetime. Therefore, these "alteration environments" have distinct differences in water chemistry, temperature, and most importantly, the water:rock ratio. Possibly, the REE behave differently in these two "alteration environments." In particular, we caution that results of alteration studies on dredged surface samples may not be applicable to basalts deeper within the crust.

2) Ludden and Thompson (in press a,b) studied whole-rock samples, whereas we separated concentrates of glass and palagonite. Their bulk rock study probably includes several alteration processes (palagonitization, formation of secondary minerals, etc.). Our study is limited to exchange reactions between hydrous solution and glass and palagonite.

3) The anomalous behaviors of Ce (Frey et al., 1974) might be explained by different compositions of hydrous solutions or redox state or by unrecognized admixture of a Ce-bearing secondary mineral in their samples.

A comparison of Cr, Hf, Sc, and Co concentrations in glass and palagonites (Table 3) indicates that these elements decrease during palagonitization in the same manner as the REE; however, Hf and Sc are not depleted in palagonite Sample 418A-73-1, 127 cm.

Alkali Metals and $^{87/86}$Sr

Glasses

We determined K, Rb, Cs, Ba, Sr, and $^{87/86}$Sr on four glass-palagonite pairs and some additional "contaminated" glass concentrates (Glass B), the results being listed in Table 4.

TABLE 4
K, Rb, Cs, Ba, Sr, and $^{87/86}$Sr in Glasses and Corresponding Palagonites
From Site 418 (concentrations in ppm)

| Sample (Interval in cm)	K	Rb	Cs	Ba	Rb/Sr	Sr	$^{87/86}$Sr
418A-15-1, 144							
Glass	993	1.49	0.015	26.4	0.0148	101.0	0.70321 ±6
Palagonite	8 800	20.2	0.407	8.07	0.264	76.5	0.70844 ±6
418A-42-3, 17							
Glass A	466	0.67	0.0096	8.66	0.0074	90.1	0.70301 ±6
Glass B	540	0.87	0.0149	7.27	0.0097	89.3	0.70346 ±6
Palagonite	12 300	23.2	0.799	64.6	0.1007	230.3	0.70760 ±9
418A-73-1, 127							
Glass A	5 270	4.37	0.0239	36.7	0.0394	110.8	0.70369 ±6
Glass B	6 460	5.44	0.0258	32.3	0.0469	116.1	0.70382 ±6
Palagonite	3 870	4.95	0.082	25.8	0.0375	131.9	0.70521 ±9
418A-86-5, 29							
Glass	2 740	2.86	0.0225	28.5	0.0257	111.1	0.70390 ±6
Palagonite	3 300	4.30	0.0404	47.0	0.0332	129.6	0.70568 ±7
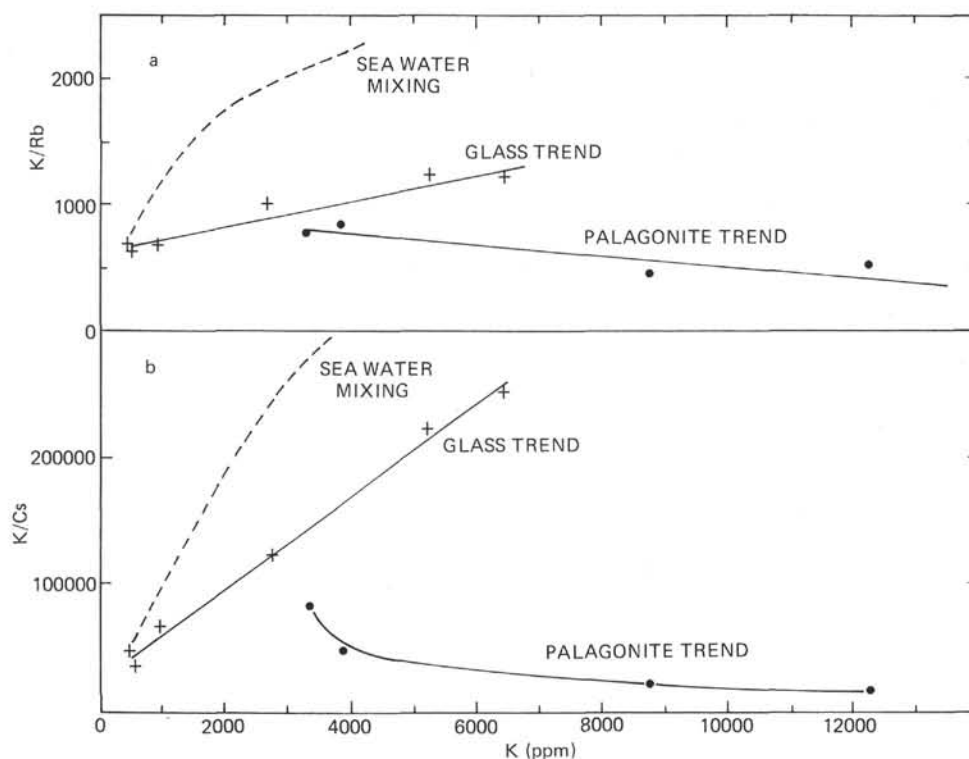
Figure 5. *K/Rb (a) and K/Cs (b) ratios versus K concentrations in glasses (crosses) and palagonites (dots). Dashed line represents the calculated trend for sea-water addition.*

The K concentrations of the microscopically fresh glass concentrates are generally higher when determined by isotope dilution than by microprobe (Byerly and Sinton, this volume). Only Sample 418A-42-3, 17 cm, Glass A, shows good agreement between microprobe (0.06% K_2O) and isotope dilution (0.056% K_2O). Rb and Cs contents in this sample are lower than those found in the other glasses. We believe that Sample 418A-42-3, 17 cm, Glass A, is the least altered and most representative of the actual liquid composition. However, even this analysis shows a comparatively high [87/86]Sr (0.70301), which may indicate slight exchange of Sr with sea water or an anomalous MORB ratio (White, 1977). The other glasses are chemically altered even though they are microscopically fresh. The following observations suggest that the alteration of glass is primarily a surface effect:

a) Byerly and Sinton (this volume) found "fresh" (low K_2O) glass for all samples, which shows that alteration is not pervasive.

b) Glass B, which contained surfaces not freshly broken, always had higher alkali concentrations than Glass A, and in one case (Section 418A-73-1) even higher than the palagonite.

c) Sample 418A-42-2, 17 cm, which yielded the "freshest" glass concentrate, was the least cracked and represented a single, large piece of glass. The other samples were intensely cracked.

Rb, Cs, Ba, and [87/86]Sr roughly increase with increasing K. To show how the alkalies vary in their relative proportions, we plotted K/Rb and K/Cs versus K in Figure 5a,b. Both K/Rb and K/Cs in glass form linear positive trends with increasing K relative to Rb and Cs increases with increasing concentration. This is different from the variation found in the palagonite concentrates; therefore, any possibility that these glass samples were contaminated with palagonite can be ruled out. We also compared these empirically determined trends with theoretically calculated trends expected from simple addition of sea-water alkalies. Figure 5a,b shows that mixing with sea-water alkalies would produce positive trends (dashed lines) *steeper* than those observed. Thus Rb and Cs are more enriched than would be expected from the simple addition of sea-water alkalies. For a given K content, we calculated a ratio of "measured" Rb or Cs to the "theoretical" (mixing) Rb or Cs: For K = 4000 ppm, this ratio is 2.6 for Rb and 2.1 for Cs. Therefore, Rb is more enriched than Cs, relative to the concentration expected from simple sea-water admixture. We conclude that the sequence of relative enrichment (K > Rb > Cs) is determined by factors other than their abundance of sea water. This sequence corresponds to that of decreasing ionic radii and is reversed from what would be expected for adsorption on clay minerals (Hart, 1969). This suggests that the glass alteration may be a diffusion-controlled process as previously proposed for palagonitization (Moore, 1966) and hydration of obsidian artifacts (Tsong et al., 1978).

These trends of K/Rb and K/Cs versus K in glasses run counter to the negative trends usually found in low-tem-

perature alteration of dredged basalts (Hart, 1969). However, Hart and Nalwalk (1970) found similar trends in glass-rich basalts from the Puerto Rico trench. Therefore, alteration of glass may be present in these samples as well.

Palagonites

The palagonites also show a systematic variation of alkali ratios versus K content (Figure 5a,b). K/Cs and K/Rb show negative trends, and the $^{87/86}$Sr shows a positive trend with increasing K; that is, Rb and Cs are enriched relative to K. The trends for K/Rb and K/Cs in palagonites run counter to those in glasses but are similar to those found in dredged pillow margins (Hart, 1969). Therefore, the trends shown by pillow margins can be recognized as being typical of palagonite-sea water exchange.

The palagonites show systematic trends with depth: K/Ba and $^{87/86}$Sr decrease, while K/Cs and K/Rb increase. This might be explained either by changing water composition, changing temperature (and, therefore, changing partition coefficients), or, since the deeper palagonites are closest to fresh-basalt composition, by a decreasing volume of sea water percolating through the rock.

The Sr concentrations in the glasses represent typical MORB values. The difference between Glasses A and B is slight compared to experimental error. We conclude there is only limited migration of elemental Sr between sea water and fresh glass even though isotopic Sr exchange has been clearly demonstrated. The palagonites, however, show significant deviations in Sr concentration, both decreasing and increasing, from the corresponding fresh glasses. Palagonite Section 418A-15-1 has lower Sr concentrations than the glass adjacent to it; therefore, Sr was "lost" during palagonitization. Nevertheless, high $^{87/86}$Sr in this sample demonstrates extensive isotopic exchange of Sr with sea water. It is interesting to note that the shallowest palagonite in the drilled section has the lowest Sr concentration, and that Section 42-3, which has the highest Sr concentration, is close to a permeable layer. In general, we find that Ba correlates with Sr.

Whole Rocks

In the previous section we recognized two sea-water alteration mechanisms which have very different effects on the alkalies. However, there are many more reactions that can be summarized as "low-temperature alteration" of basalts, viz., alteration of individual minerals, addition of vein material, and migration along grain boundaries. All of these reactions may influence the abundance of elements in a largely crystalline whole-rock sample. Alteration processes may also vary as a function of the geologic setting (for example, whether or not a sample is close to the surface or to a permeable layer) or as a function of the composition and temperature of pore fluids. Because many processes and geologic parameters affect the data obtained on whole rocks, a comparatively poor correlation of alteration-sensitive parameters is not unexpected.

Our data on K, Rb, Cs, Ba and $^{87/86}$Sr from whole-rock samples are presented in Table 5. On the basis of alteration-sensitive parameters (K_2O, H_2O, Fe_2O_3, $^{87/86}$Sr), the two freshest rocks are Sections 417D-69-1 and 418A-18-4. Since these and the fresh Section 418A-42-3 (Glass A) have

about the same K content, we can calculate average fresh-alkali and alkaline-earth contents for these least-altered basalts:

	Least-Altered Hole 418A Basalts	Average MORB[a]
K (ppm)	450	1064
Rb (ppm)	0.483	1.02
Cs (ppm)	0.00940	0.0131
Sr (ppm)	100	124
Ba (ppm)	8.46	12.2
K/Rb	932	1046
K/Cs	47,800	81,000
K/Ba	53.2	109
^{87}Sr/^{86}Sr	0.70325	0.70265

[a]Hart (1976).

Compared to average MORB, the least-altered 418A basalts are significantly depleted in alkalies and slightly depleted in Sr and Ba. Alteration effects in even these least-altered samples are suggested by the low K/Cs and the high $^{87/86}$Sr ratios. The latter are particularly significant, as MORB typically have ratios less than 0.7030 (Hart, 1976) whereas all of the Hole 418A samples (including the freshest glass and the acid-leached, whole-rock sample) have $^{87/86}$Sr ratios greater than 0.7030. In this respect, these samples are similar to an anomalous highly depleted fresh glass analyzed by White (1977) from the Mid-Atlantic Ridge (at 33.4°N), which had very low contents of K, Rb, Cs, and Ba, coupled with a $^{87/86}$Sr ratio of 0.7034. If these are primary geochemical features, they are phenomena that are rare and poorly understood.

It is obvious from Figures 5a,b and 6a,b that both glass and palagonite data fit to very well defined trends, while the whole-rock data scatter considerably. This implies that the exchange of sea water with glass and palagonite represents single, well-defined processes of alteration, whereas the variation of the whole-rock data is caused by a combination of processes. Most of the whole-rock data can be accounted for as reflecting various mixtures of fresh MORB, palagonite, altered glass, and secondary minerals (secondary mineral data are discussed in Hart and Staudigel, 1978). Some of our most-altered samples (Sections 417D-49-2, 418A-56-6, and 418A-65-1) are taken close to the glassy margins of pillows and therefore have high glass (palagonite) contents. These samples fall very closely along the trend defined by the compositions of palagonite *concentrates*, indicating that palagonite formation is the most important process for the alteration of these rocks. Samples which are more crystalline (e.g., Section 418A-76-2) tend to fall within, or close to, the fresh-rock composition.

However, there are some anomalous compositions of palagonite-rich samples which deviate appreciably from the trends for palagonites (Figure 6b): Section 418A-41-3 has a K concentration significantly higher, and Section 418A-47-3 significantly lower, than expected from the palagonite trend. This divergence may reflect either a complex alteration process or it may be related to the geologic

TABLE 5
K, Rb, Cs, Ba, and $^{87/86}$Sr in Basalts From Sites 417 and 418 (concentrations in ppm)

Sample (Interval in cm)	K	Rb	Cs	Ba	Sr	Rb/Sr	$^{87/86}$Sr
417D-26-3, 40	3 630	4.16	0.038	8.21	115	0.0359	0.70365 ±8
417D-49-2, 23	2 970	5.69	0.078	8.89	118	0.0482	0.70349 ±6
417D-60-6, 50	696	0.32	–	5.47	115	0.0028	0.70385 ±6
417D-69-1, 122	454	0.37	0.0091	9.57	98	0.0038	0.70333 ±6
418A-15-2, 0	2 960	3.02	0.034	10.9	114	0.0265	0.70355 ±7
418A-17-3, 40	1 172	1.33	0.014	13.9	121	0.0110	0.70358 ±6
418A-18-4, 40	432	0.41	0.0095	7.14	111	0.0037	0.70342 ±6
418A-22-1, 46	–	–	–	–	113[a]	–	0.70376 ±5
418A-41-3, 100	11 260	9.48	0.117	5.65	376	0.0252	0.70614 ±6
418A-42-3, 68	1 860	2.31	0.373	30.80	117	0.0197	0.70426 ±5
Leached							0.70313 ±11
418A-56-6, 82	7 240	21.50	0.413	45.6	75		0.70761 ±7
418A-57-2, 112	1 040	2.96	0.033	7.51	106	0.0279	0.70378 ±5
418A-62-4, 104	1 870	3.84	0.056	3.84	116	0.0331	0.70357 ±5
418A-64-4, 82	632	1.45	–	7.89	112	0.0129	0.70366 ±8
418A-65-1, 108	11 730	30.98	0.867	–	179		0.70686 ±5
418A-69-3, 63	1 085	1.56	0.023	16.87	109	0.0143	0.70347 ±9
418A-73-1, 127	–	–	–	–	105[a]		0.70318 ±5
418A-76-1, 4	1 990	1.45	0.0156	17.12	122	0.0119	0.70361 ±6
418A-76-2, 99	880	2.55	0.0301	25.27	127	0.0201	**0.70432 ±4**
418A-86-5, 29	592.9	1.07	0.0143	5.77	108	0.0099	0.70365 ±7

[a]Data obtained by XRF.

setting of the samples. Core 41 represents a major period of volcanic quiescence (Robinson et al., this volume). Because the oceanic crust forms most of its secondary minerals shortly after its formation (Hart and Staudigel, 1978), Core 41 probably reflects a major thermal boundary as well. After extrusion of the youngest lavas at Hole 418A, the section below Core 41 may have been relatively warm because previously formed vein material decreased the hydrothermal circulation and the overlying basalts insulated it from cold sea water. The pillows and flows above Core 41 may have been relatively cold, since they were efficiently cooled by fast hydrothermal circulation. The anomalously high K sample Section 418A-41-3 derives from this cold section, whereas the low K samples come from the warm, lower section. A similar geologic setting might account for the unusually high K contents in Hole 417A basalts (Donnelly and Francheteau, 1977). Hole 417A was drilled into a topographic hill, which may have been very open to circulation of cold sea water and therefore created a similar trap for K.

Whole-rock Sr concentrations are relatively unaffected by alteration and are similar to "fresh" MORB abundances, but both lower and higher values are frequently observed. Sr behaves like Ca in these rocks: high Sr is usually accompanied by high CO_2 and Ca contents, indicating Sr addition to the rock as Sr-carbonate (data from Staudigel et al., this volume). Low Sr content and high $^{87/86}$Sr (e.g., Sample 418A-56-6, 82 cm) indicate simultaneous removal of Sr and exchange with sea-water Sr. Therefore, as observed for Ca (Staudigel et al., this volume), Sr can be both added (e.g., as carbonate) and leached from the rock during low-temperature alteration.

SUMMARY

Chondrite-normalized REE distributions of Hole 417D and 418A basalts show relative LREE-depleted patterns typical of MORB. K, Rb, Cs, Sr, and Ba concentrations are significantly lower than average MORB. However, $^{87/86}$Sr ratios of these basalts are > 0.7030 and thus significantly higher than MORB. This can be interpreted as an effect of alteration or as an anomalous primary feature. Comparisons of compositions of hand-picked glass and palagonite concentrates reveal two alteration processes with distinct compositional variations:

1) *Glass-sea water exchange,* a diffusive surface alteration of glass without microscopic effects of palagonitization, causes increased K/Rb and K/Cs with increasing K content. REE contents are not affected.

2) *Palagonite formation* causes significant losses of REE up to 40 wt. % without influencing relative abundances. In contrast to the trends of Type 1 alteration, K/Rb and K/Cs ratios in palagonites decrease with increasing K content. Therefore, the Type 1 alteration process is distinct from palagonite formation. Palagonite does not represent a unique alteration product of basaltic glass. It is rather represented by a compositional range with distinct chemical trends.

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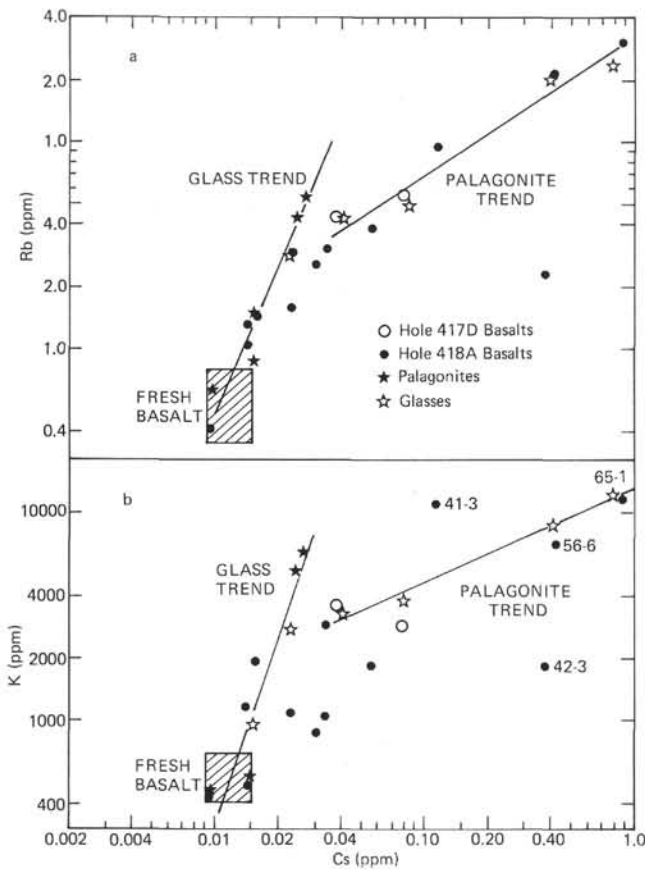
Figure 6. *Rb versus Cs (a) and K versus Cs (b) in whole-rock samples from Sites 417 and 418. For comparison purposes, data for glasses and palagonites are plotted as well.*

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